

Theoretical Derivation of Stable and Nonisotopic Approaches for Assessing Soil Organic Carbon Turnover

D. E. Clay,* C. G. Carlson, S. A. Clay, C. Reese, Z. Liu, J. Chang, and M. M. Ellsbury

ABSTRACT

Techniques for measuring soil organic C (SOC) turnover in production fields are needed. The objectives of this study were to propose and test nonisotopic and ^{13}C stable isotopic techniques for assessing SOC turnover. Based on SOC equilibrium and mass balance relationships, an equation was derived: $\text{NHC}/\text{SOC}_{\text{initial}} = [1/(\text{SOC} \times k_{\text{NHC}})] (\text{dSOC}/\text{dt} + k_{\text{SOC}}/k_{\text{NHC}})$, where dSOC/dt is the annual change in SOC, NHC is nonharvested C returned to soil, k_{SOC} is the annual mineralization rate of SOC, and k_{NHC} is the annual mineralization rate of NHC. This equation was used to calculate maintenance rates. An isotopic approach based on simultaneously solving the equations was developed to determine C budgets: (i) $\text{SOC}_{\text{retained}} = [\text{SOC}_{\text{final}} (\Delta_{\text{soil final}} - \Delta_{\text{PCR}})/(\Delta_{\text{SOC retained}} - \Delta_{\text{PCR}})]$; (ii) $\Delta_{\text{SOC retained}} = \Delta_{\text{SOC initial}} - [\varepsilon \ln(\text{SOC}_{\text{retained}}/\text{SOC}_{\text{initial}})]$; (iii) $\Delta_{\text{PCR}} = \Delta_{\text{NHC}} - [\varepsilon \ln(\text{PCR}/\text{NHC})]$; and (iv) $\text{SOC}_{\text{final}} = \text{SOC}_{\text{retained}} + \text{PCR}_{\text{incorp}}$, where ε is the Rayleigh fractionation constant, $\text{PCR}_{\text{incorp}}$ is the amount of NHC incorporated into SOC_{final} with Δ_{PCR} being the associated ^{13}C discrimination (Δ) value, and $\text{SOC}_{\text{retained}}$ is the amount of SOC_{initial} retained in the soil after mineralization with $\Delta_{\text{SOC retained}}$ being the associated Δ value. Isotopic and nonisotopic approaches were tested on a production field where aboveground corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] yields were measured with a yield monitor and soil samples collected from a slightly offset grid (30 m) in 1995 and 2003 were analyzed for organic C and Δ . The nonisotopic approach showed that maintenance rates increased with SOC and that an accurate measure of NHC was required to calculate maintenance requirements. Sensitivity analysis of the isotopic approach showed that calculated budgets were sensitive to ^{13}C discrimination during SOC mineralization. If ^{13}C discrimination during SOC and NHC mineralization did not occur ($\varepsilon = 0$), then 14.9 and 7.6% of the SOC measured in 1995 ($\text{SOC}_{\text{initial}}$) was mineralized, and 7420 and 2780 kg C ha⁻¹ of NHC were incorporated into SOC_{final} in the 523.4- to 527.3- and 527.3- to 529.2-m elevation zones, respectively. If ^{13}C discrimination occurred ($\varepsilon = -2.52\text{‰}$) during SOC mineralization, then the calculated amount of SOC mineralized and the amount of new C incorporated into SOC were reduced.

To reduce our dependence on fossil fuels, it has been proposed that most of the aboveground corn biomass be harvested for ethanol production. To ensure that corn stover harvesting does not degrade the soil resource, SOC inputs must equal outputs. The current

approaches for defining C budgets and maintenance rates have limitations (they require a reference site, do not consider ^{13}C discrimination during mineralization, and are difficult to apply to the whole field) that reduce their usefulness at field and watershed scales.

Both isotopic and nonisotopic approaches have been used to define SOC dynamics. Nonisotopic approaches have relied on changes in nonharvested biomass C returned to the soil or changes in tillage to produce changes in SOC (Larson et al., 1972; Barber, 1979; West and Post, 2002). Based on these changes, the amount of nonharvested biomass returned to the soil required to maintain SOC are calculated. Major disadvantages with the nonisotope approach are that C losses and gains are determined by subtracting two large numbers (initial and final SOC values) containing large spatial variability, SOC derived from C₄ and C₃ plants cannot be separated, and measuring belowground biomass is difficult.

The ^{13}C stable isotope approach has been used to separate SOC into C derived from C₃ and C₄ plants. This approach relies on the observation that C₃ and C₄ plants have different Δ values. While C₃ plants typically have Δ values ranging from 17 to 20‰, C₄ plants have Δ values ranging from 2.5 to 4‰ (Clay et al., 2001b, 2003). Based on isotopic differences between C₃ and C₄ plants, a mixing equation [$f = (\Delta_{\text{SOC}} - \Delta_{\text{C}_4})/(\Delta_{\text{C}_3} - \Delta_{\text{C}_4})$] has been used to calculate the relative proportion of C₃ and C₄ biomass contained in SOC (Huggins et al., 1998; Allmaras et al., 2000; Clapp et al., 2000; Layese et al., 2002; Allmaras et al., 2004). By repeated sampling, the rate of change in the SOC derived from C₃ and C₄ plants is determined. This approach works best when a soil derived from C₃ plants is switched to C₄ plants or vice versa. These calculations assume that ^{13}C fractionation during mineralization does not occur. If this approach is combined with experiments containing paired treatments, i.e., residue removed and returned, then by subtraction the SOC derived from stover and roots can be calculated (Allmaras et al., 2004). Disadvantages are that many years are required to conduct these experiments, potential fractionation must be considered, and turnover rates cannot be calculated if the rotation includes both C₃ and C₄ plants.

Changes in C storage can also be determined in systems where the species composition or management has changed (Balesdent and Mariotti, 1996). This approach requires a reference site where the original vegetation or management is maintained. Calculations are based on Δ differences in the perturbed and unperturbed sites [$F = (\Delta_{\text{soil final}} - \Delta_{\text{soil reference final}})/(\Delta_{\text{vegetation}} - \Delta_{\text{vegetation reference}})$]. By repeated sampling, this approach is a direct expression

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Abbreviations: Δ , ^{13}C discrimination value; NHC, nonharvested C; PCR, plant biomass C remaining in the soil; SOC, soil organic C.

of the turnover rate relative to the reference. Disadvantages are that an appropriate reference site must be maintained, and calculated values are not absolute and are relative to the reference site.

The data and treatment requirements of the current approaches for assessing SOC dynamics make them unsuitable for assessing SOC dynamics in many production fields. The objectives of this study were to propose and test nonisotopic and ^{13}C stable isotopic techniques for assessing SOC turnover.

MATERIALS AND METHODS

Method Development

Theoretical Derivation of Nonisotopic Approach

Based on a summary of data presented by West and Post (2002), Allmaras et al. (2004), Clapp et al. (2000), and Wilhelm et al. (2004), it can be derived that at or near the SOC equilibrium point (SOC_e),

$$k_{\text{SOC}}(\text{SOC}_e) = k_{\text{NHC}}\text{NHC}_m \quad [1]$$

$$d\text{SOC}/dt = k_{\text{NHC}}(\text{NHC}_a - \text{NHC}_m) \quad [2]$$

$$\text{NHC}_a = \text{NHC}_m + (\text{NHC}_a - \text{NHC}_m) \quad [3]$$

where k_{SOC} is the annual mineralization rate ($\text{kg C ha}^{-1} \text{ yr}^{-1}$) of SOC, k_{NHC} is the annual mineralization rate of nonharvested C ($\text{kg C ha}^{-1} \text{ yr}^{-1}$) returned to the soil, NHC_m is the amount of nonharvested C required to maintain SOC at SOC_e (kg ha^{-1}), $d\text{SOC}/dt$ ($\text{kg C ha}^{-1} \text{ yr}^{-1}$) is the annual change in soil organic C ($\text{kg C ha}^{-1} \text{ yr}^{-1}$), and NHC_a (kg ha^{-1}) is the total amount of nonharvested C returned to the soil (kg ha^{-1}). By solving for NHC_m in Eq. [1], substituting this value [$\text{SOC}_e(k_{\text{SOC}}/k_{\text{NHC}})$] for NHC_m in Eq. [3], solving for $(\text{NHC}_a - \text{NHC}_m)$ in Eq. [2], substituting this value [$(1/k_{\text{NHC}})(d\text{SOC}/dt)$] for $[\text{NHC}_a - \text{NHC}_m]$ in Eq. [3], and dividing both sides by SOC_e , the equation

$$\text{NHC}_a/\text{SOC}_e = [1/(k_{\text{NHC}}\text{SOC}_e)](d\text{SOC}/dt) + k_{\text{SOC}}/k_{\text{NHC}} \quad [4]$$

was derived. If $\text{SOC}_{\text{initial}}$ is near SOC_e , then $\text{SOC}_{\text{initial}}$ is approximately equal to SOC_e , resulting in the equation

$$\text{NHC}_a/\text{SOC}_{\text{initial}} = [1/(k_{\text{NHC}}\text{SOC}_{\text{initial}})](d\text{SOC}/dt) + k_{\text{SOC}}/k_{\text{NHC}} \quad [5]$$

This equation was rewritten into

$$\text{NHC}_a/\text{SOC}_{\text{initial}} = m(d\text{SOC}/dt) + b \quad [6]$$

which can be solved using linear regression. The values of NHC_m , k_{NHC} , and k_{SOC} are calculated using the equations

$$\text{NHC}_m = b\text{SOC}_{\text{initial}} \quad [7]$$

$$k_{\text{NHC}} = 1/(m\text{SOC}_{\text{initial}}) \quad [8]$$

$$k_{\text{SOC}} = b/(m\text{SOC}_{\text{initial}}) \quad [9]$$

Isotopic-Based Carbon Budgets

An approach for calculating SOC budgets for systems containing both C_3 and C_4 plants is described below. The approach is based on changes in soil Δ with time, the Δ value

of added plant material, and modeling. This approach can be used to determine SOC dynamics at specific points. By mass balance, the Δ value of SOC at the end of an experiment ($\Delta_{\text{soil final}}$) was defined as

$$\Delta_{\text{soil final}} = \frac{\text{PCR}_{\text{incorp}}(\Delta_{\text{PCR}}) + \text{SOC}_{\text{retained}}(\Delta_{\text{SOC retained}})}{\text{PCR}_{\text{incorp}} + \text{SOC}_{\text{retained}}} \quad [10]$$

where $\text{PCR}_{\text{incorp}}$ is the plant C retained in the soil that was incorporated into SOC, Δ_{PCR} is the Δ value of the plant material retained in the soil after mineralization (for calculations see below), $\text{SOC}_{\text{retained}}$ is the amount of old C ($\text{SOC}_{\text{initial}}$) retained in the soil at the end of the study, and $\Delta_{\text{SOC retained}}$ is the associated Δ value. By mass balance $\text{SOC}_{\text{final}}$ is

$$\text{SOC}_{\text{final}} = \text{PCR}_{\text{incorp}} + \text{SOC}_{\text{retained}} \quad [11]$$

By simultaneously solving Eq. [10] and [11], the equation

$$\text{SOC}_{\text{retained}} = \frac{\text{SOC}_{\text{final}} (\Delta_{\text{soil final}} - \Delta_{\text{PCR}})}{\Delta_{\text{SOC retained}} - \Delta_{\text{PCR}}} \quad [12]$$

was derived. This equation can be rearranged into the form $\text{PCR}_{\text{incorp}} = \text{SOC}_{\text{final}}(\Delta_{\text{soil final}} - \Delta_{\text{SOC retained}})/(\Delta_{\text{PCR}} - \Delta_{\text{SOC retained}})$. This expression is similar to Eq. [2] reported by Balesdent and Mariotti (1996), and the equation $\text{SOC}_{\text{corn}} = (\text{SOC}_{\text{final}})(\Delta_{\text{soil final}} - \Delta_{\text{soil initial}})/(\Delta_{\text{corn stover}} - \Delta_{\text{soil initial}})$ used by Clapp et al. (2000) and Allmaras et al. (2004). Differences between the two equations are beyond the scope of this study and are discussed in Balesdent et al. (1988) and Balesdent and Mariotti (1996).

If ^{13}C discrimination during mineralization occurs, then Balesdent and Mariotti (1996) reported that $\Delta_{\text{SOC retained}}$ was calculated with the Rayleigh fractionation equation: $\Delta_{\text{SOC retained}} = \{[\Delta_{\text{SOC initial}} - (\epsilon \ln(\text{SOC}_{\text{retained}}/\text{SOC}_{\text{initial}}))]\}$. The ϵ value represents a Rayleigh isotopic fractionation constant. If ϵ is equal to zero (no isotopic discrimination), then $\Delta_{\text{SOC retained}}$ simplifies to $\Delta_{\text{SOC initial}}$ and Δ_{PCR} simplifies to the Δ value of the added plant material. Evidence supporting isotopic discrimination during mineralization is mixed. Santruckova et al. (2000) reported that $\delta^{13}\text{C}$ of respired CO_2 was similar to the $\delta^{13}\text{C}$ value of SOC and Connin et al. (2001) reported that ^{13}C isotopic discrimination is characteristic of early litter decay in arid environments. Balesdent and Mariotti (1996) summarized the unpublished work of M. Linères (1996), in which the $\delta^{13}\text{C}$ value of the initial corn biomass did not change after 85% of the biomass had been mineralized. During the mineralization of trichlorobenzene, stable ^{13}C isotope fractionation was not observed under aerobic conditions but was observed under anaerobic conditions (Griebler et al., 2004). Cleveland et al. (2004) reported that the $\delta^{13}\text{C}$ signatures of dissolved organic matter did not change during decomposition. Fernandez and Cadisch (2003) reported that, with time, fractionation may even out, with microbes discriminating against ^{13}C (relative to the initial label) during early stages followed by a period of time when microbes discriminate against ^{12}C (relative to the initial label). Balesdent and Mariotti (1996) reported that, based on temporal changes in $\delta^{13}\text{C}$ and SOC for 70 yr in fallowed plots located in France, ϵ was calculated to be -1.71% . Carbon budgets were developed by simultaneously solving Eq. [11] and [12] and the Rayleigh fractionation equation. The amount of initial C lost during the study was then calculated using the equation

$$\text{SOC}_{\text{initial lost}} = \text{SOC}_{\text{initial}} - \text{SOC}_{\text{retained}} \quad [13]$$

The sensitivity of the approaches was tested using a range of root/shoot ratios. Although only C budgets where $\epsilon = 0$ are reported here, the sensitivity of calculated C budgets to ϵ was investigated.

Table 1. Cultural and climatic information for the study area between 1995 and 2002.

Year	Crop	Planting	Harvest	Precipitation	gdd†	Fertilizer applied		Tillage	Row spacing
						N	P		
				cm	°C	— kg ha ⁻¹ —			cm
1995	corn	21 May	9 Nov.	82	1130	119	26	no-till	53
1996	soybean	17 May	5 Oct.	51	1040	0	0	no-till	18
1997	corn	28 Apr.	27 Oct.	41	1140	154	37	no-till	53
1998	soybean	7 May	30 Oct.	48	1340	0	0	no-till	18
1999	corn	29 Apr.	21 Oct.	52	1160	190	46	no-till	53
2000	soybean	2 May	27 Sept.	57	1180	0	0	strip-till	18
2001	corn	4 May	20 Oct.	58	1290	179	78	strip-till	53
2002	corn	4 May	4 Nov.	59	1390	151	66	strip-till	53

† Growing degree days.

Field Experiment

Data between 1995 and 2003 from a site located in east-central South Dakota in a 65-ha field located at 44°10'N and 96°37'W were used to test the approaches described above. Corn was sown in 1995, 1997, 1999, 2001, and 2002, and soybean was sown in 1996, 1998, and 2000. Cultural practices are shown in Table 1. To reduce residue interference with corn following corn (2001 and 2002), between 50 and 75% of the corn stover in 2001 was chopped, windrowed, baled, and removed. Residue was not removed between 2002 and 2003. The amounts of N and P fertilizer applied, growing degree days (base 10°C), varieties, and precipitation for each study year are summarized in Table 1. Tile lines were repaired between 1996 and 1997. For comparative purposes, oven-dry soybean and corn dry weights are reported. Selected soil chemical and physical properties at the site were summarized in Clay et al. (2001a, 2001b, 2004). Corn and soybean Δ values for different elevations were reported by Clay et al. (2001b, 2003).

Soil samples from the 0- to 15-cm soil depth were collected from a 30- by 30-m offset grid in May 1995 and between May and June in 2003. Each sample was a composite that contained 15 individual 1.7-cm-diam. cores collected every 11.4 cm along a transect. Soil samples were air dried (35°C), ground, sieved (2-mm sieve), and analyzed for total N, total C, $\delta^{15}\text{N}$, and Δ on a ratio mass spectrometer (Clay et al., 2001b). Total C was corrected for inorganic C (Loeppert and Suarez, 1996). The values of Δ and $\delta^{15}\text{N}$ were calculated using the equations

$$R = {}^{13}\text{C}/{}^{12}\text{C} \quad [14]$$

$$\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1)1000\text{‰} \quad [15]$$

$$\Delta = (\delta^{13}\text{C}_a - \delta^{13}\text{C}_p)/(1 + \delta^{13}\text{C}_p/1000) \quad [16]$$

$$\delta^{15}\text{N} = ({}^{15}\text{N}/{}^{14}\text{N}_{\text{sample}} - {}^{15}\text{N}/{}^{14}\text{N}_{\text{standard}})/({}^{15}\text{N}/{}^{14}\text{N}_{\text{standard}})1000\text{‰} \quad [17]$$

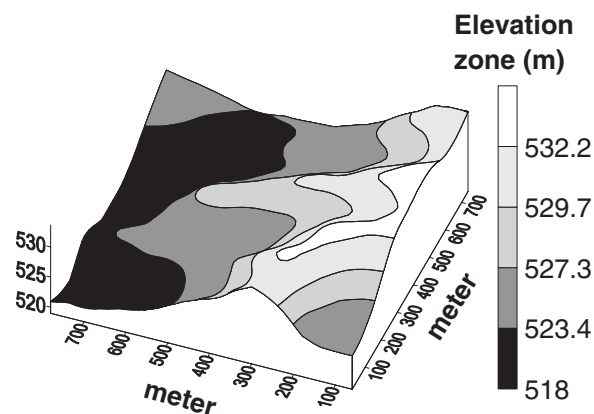
where limestone from the Pee Dee formation in South Carolina was used as the R_{standard} for C, $\delta^{13}\text{C}_a$ is the ${}^{13}\text{C}$ natural abundance for air (−8‰), $\delta^{13}\text{C}_p$ is the ${}^{13}\text{C}$ natural abundance for the sample, and 0.0036765 (air) was used for ${}^{15}\text{N}/{}^{14}\text{N}_{\text{standard}}$ (O'Leary, 1993).

More than 600 soil samples were collected at each sampling date in 1995 and 2003. The soil samples from each year were aggregated to a common 40- by 40-m grid cell. The value of a grid cell was calculated as the average value of all the samples contained within a cell. A grid cell SOC value was the difference between inorganic (measured on the 1995 data set) and total C. The grid cells were separated into five elevation-based management zones (<523.4, 523.4–527.3, 527.3–529.74, 529.74–532.2, and 532.2–534.30 m, Fig. 1).

Quantification of Yield and Carbon Inputs

Fifty geographically representative sites along four transects were identified for characterizing temporal and spatial yield variability. Corn stover was hand harvested from 2.29 m of row at each site in 1995, 1997, 1999, 2001, and 2002. Corn grain yields at these sites were measured and spatially located by a combine equipped with a calibrated yield monitor and differentially corrected global positioning system (DGPS). The combine head was 4.2 m before 2002 and 6.1 m after 2002. To ensure yield monitor data accuracy, data points were removed from the data set if the combine speed was slower than 1.78 m s⁻¹, faster than 3.05 m s⁻¹, or if the flow rate exceeded ± 3 standard deviations of the average flow rate. In 2002, corn grain yields were determined by hand harvesting 4.58 m of row. Corn grain and stover samples were dried, ground, and analyzed for total N, $\delta^{15}\text{N}$, total C, and Δ as described above. Based on the measured C content of the corn stover, which ranged from 40 to 42%, biomass C was calculated by multiplying nonharvested biomass by 0.409.

In 1996, 1998, and 2000, soybean yields were measured at the 50 sites described above with a calibrated yield monitor equipped with DGPS. The soybean head on the combine was 9.1 m. Soybean grain samples were collected by hand from 1-m² areas at the 50 representative sampling points in 2000. These samples were analyzed for total N, $\delta^{15}\text{N}$, total C, and Δ as described above. Based on related experiments conducted in this field or at nearby sites in 1999, 2000, 2001, and 2002, nonharvestable (leaves, pods, and stalks) materials were estimated using a measured harvest index of 0.35 (grain/nonharvestable material). Grain, leaf, and stalk samples were analyzed for organic C and Δ . Based on measured soybean leaves and stalks, which ranged from 40 to 41%, nonharvestable biomass C was calculated by multiplying biomass re-

**Fig. 1. The location of the elevation-zone boundaries in the field.**

turned by 0.405. Carbon inputs and yields were determined for the elevation-based management zones described above.

Belowground productivity has been estimated from above-ground productivity using the equation

$$\text{Net belowground productivity} = k(\text{net aboveground productivity}) \quad [18]$$

Wilts et al. (2004) reported that, for corn, k values ranged from 1.14 to 1.17. Some studies have reported lower values (Buyanousky and Wagner, 1997; Clapp et al., 2000) while other studies have reported higher values (Allmaras et al., 2004). Different k values are the direct result of different techniques used to measure belowground biomass. Approaches that measure root exudates have higher k values than approaches that do not measure exudates (Bolinder et al., 1999). Plant data were aggregated to the five elevation-based management zones. Means, standard deviations, and 90% confidence intervals were calculated and semivariances of the SOC and Δ values were determined. For corn, belowground biomass was determined for a range of root/shoot ratios (none, 0.0; low, 0.4; moderate, 0.8; and high, 1.5). For soybean, belowground biomass was simulated using a slightly different range of root/shoot ratios (none, 0.0; low, 0.4; moderate, 1.00; and high, 1.5).

A mixing equation as described by Allmaras et al. (2004) was used to calculate the relative contribution of soybean (f) and corn ($1 - f$) plants to SOC. The amount of SOC derived from C_3 (SOC_{C3}, from soybean) or C_4 (SOC_{C4}, from corn) was calculated by multiplying SOC by f and $(1 - f)$, respectively. Equations [11] and [12] were used to calculate the amount of SOC mineralized (SOC_{initial lost}) the amount of initial SOC retained in the soil after mineralization, and new C that was incorporated into the SOC (PCR_{incorp}).

To solve Eq. [12], a value for Δ_{PCR} was required. This value was calculated using the equation

$$\Delta_{\text{PCR}} = \frac{\sum_{t=1}^8 (\text{PCR}_{C4-C,t} \Delta_{\text{PCR } C4,t} + \text{PCR}_{C3-C,t} \Delta_{\text{PCR } C3,t})}{\sum_{t=1}^8 (\text{PCR}_{C4-C,t} + \text{PCR}_{C3-C,t})} \quad [19]$$

where $\text{PCR}_{C4-C,t}$ is C_4 biomass C (kg) applied in year t remaining in the soil after mineralization and $\Delta_{\text{PCR } C4,t}$ is the associated Δ value of this biomass, PCR_{C3-C} is C_3 biomass C (kg) applied in year t remaining in the soil after mineralization and $\Delta_{\text{PCR } C3,t}$ is the associated Δ value, and PCR is defined below. The $\Delta_{\text{PCR } C3,t}$ and $\Delta_{\text{PCR } C4,t}$ values are landscape specific. For example, based on measured corn stover Δ values in 2001 and 2002, the Δ_{C4} used in Eq. [4] ranged from 3.5‰ (elevation zones <523.4 m) to 3.92‰ (elevation zones >532.2 m) (Clay et al., 2001b), and based on soybean grain Δ values in 2000 that were partially reported in Clay et al. (2003), the input values used for Δ_{C3} in Eq. [19] ranged from 19.93‰ (elevation zones <523.4 m) to 18.72‰ (elevation zones >532.2 m). The $\Delta_{\text{PCR } C4,t}$ and $\Delta_{\text{PCR } C3,t}$ values in Eq. [19] were estimated using the equations

$$\Delta_{\text{PCR } C4,t} = \Delta_{C4,t} - \epsilon \ln(\text{PCR}_{C4-C,t}/\text{BP}_t) \quad [20]$$

$$\Delta_{\text{PCR } C3,t} = \Delta_{C3,t} - \epsilon \ln(\text{PCR}_{C3-C,t}/\text{BP}_t) \quad [21]$$

In Eq. [20] and [21], ϵ is the Rayleigh fractionation coefficient, which was assumed to be zero, $\Delta_{C4,t}$ is the Δ value of C_4 biomass from year t , $\Delta_{C3,t}$ is the Δ value of C_3 biomass from year t , BP_t is the nonharvested biomass C (kg) returned to the soil in year t (Balesdent and Mariotti, 1996). The $\text{PCR}_{C4-C,t}$ and $\text{PCR}_{C3-C,t}$ values in Eq. [19], [20], and [21] were calculated using the double exponential model

$$\text{PCR}_t = \text{NHC}_{a,t} - A \exp(-kt) + C \exp(-ht) \quad [22]$$

where $\text{NHC}_{a,t}$ represents the nonharvested biomass C returned to the soil in any given year, PCR_t represents the amount of plant C remaining in the soil after mineralization, A represents the percentage of easily decomposable plant C, and k is the associated decomposition rate constant of pool A, C represents the percentage of biomass that was resistant to mineralization, and h is the associated rate constant of pool C. The A , k , C , and h values, based on data reported by Buyanousky and Wagner (1997) and Angers and Chenu (1997), were 79.6%, 0.003271 d, 20.73%, and 0.000433 d, respectively. This model predicted that 41.8, 12.8, and 6.1% of the biomass mass added in 2002, 1999, and 1995, respectively, was retained in the soil in June of 2003. Even though short-term mineralization rates are plant-type dependent (Trinsoutrot et al., 2000), this study used the same model to estimate corn and soybean biomass remaining in the soil during the 8-yr period. This assumption was based on the lack of long-term (at least 8 yr) field mineralization data to dispute this simplification.

Based on Eq. [19], [20], and [21], the estimated Δ_{PCR} values in the moderate root/shoot ratio treatment were 6.36, 6.28, 6.47, 6.50, and 6.47‰ for the <523.4, 523.4- to 527.3-, 527.3- to 529.7-, 529.7- to 532.2-, and 532.2- to 534.3-m elevation zones. The high and low root/shoot ratios were within 0.3‰ of these values. For the isotopic approach, root/shoot ratio influence on calculated C budgets was limited to their impact on Δ_{PCR} .

RESULTS AND DISCUSSION

Effects on Carbon Dynamics

In 1995, SOC ranged from 48 760 kg C ha⁻¹ in the 532.2- to 534.3-m zone to 52 600 kg C ha⁻¹ in the <523.4-m zone; Δ ranged from a low value of 9.04‰ in the 527.3- to 529.7-m zone to a high value of 9.72‰ in the 529.7- to 532.2-m zone. The Δ values of these zones decreased during the 8 yr of the study, resulting in Δ values of 8.98 and 9.06‰ in the 527.3- to 529.7- and 529.7- to 532.2-m zones, respectively. Total soil N ranged from a high of 2.55 g kg⁻¹ in the elevation zone <523.4 m to a low of 2.41 g kg⁻¹ in the elevation zone >529.7 m. Decreases in SOC and total soil N with increasing elevation were attributed to erosion, which transported organic matter from summit and shoulder areas to foot-slope areas, and lower water contents in summit and shoulder areas than footslope and toestope areas, which reduced biomass production and the amount of biomass returned to the soil.

Soil organic C and Δ values in 1995 contained a substantial amount of spatial variability (Fig. 2). For Δ , the semivariance value at 40 m was ~50% of the value at 300 m. For SOC, spatial variability was also observed, with the semivariance values at 40 m being 54% of the sill. Changes in Δ during the 8 yr of the study were spatially variable and had a linear semivariogram of $y = 0.093 + 0.0001483x$, $r^2 = 0.88$ at $P = 0.01$, where y is the semivariance value (‰) and x is distance (m). Backslope and shoulder areas had relatively constant Δ values from 1995 to 2003, whereas relatively large changes in Δ were observed in elevation zones <523.4 m (Fig. 3). Spatial variability in SOC and Δ were driven by landscape and management processes that influenced SOC and Δ values.

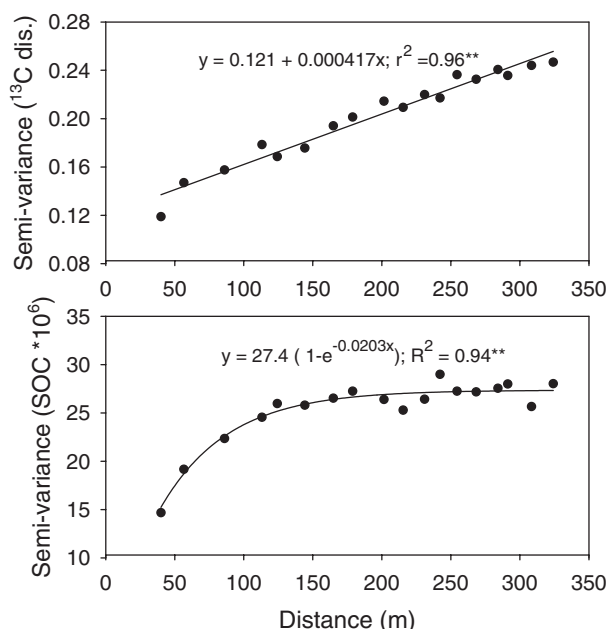


Fig. 2. Semivariograms for SOC (soil organic C) and soil ^{13}C discrimination for 1995. Units for SOC are kilograms C per hectare and units for ^{13}C discrimination are per-thousand.

Organic Carbon Inputs

Crop yields and the amount of biomass C returned to the field were influenced by spatial and temporal variability. The lowest corn yields were measured in the cool wet year of 1995 (3660–4330 kg biomass grain ha^{-1}) and the highest yields (7190–10 5560 biomass grain kg ha^{-1}) were measured in 2002 (Table 1). Soybean grain yields had similar temporal variability and averaged 1410, 2240, and 2510 kg ha^{-1} in 1996, 1998, and 2000, respectively. The low yields in 1996 were associated with cool and wet conditions (Table 1), while high yields in 2000 were attributed to timely precipitation.

Estimated nonharvested C returned to soil was higher for corn than soybean and was influenced by elevation zone and root/shoot ratio (Table 2). For the moderate root/shoot ratio, the average estimated amount of above- and belowground organic C returned to the soil by corn ranged from 6930 to 8170 $\text{kg C ha}^{-1} \text{yr}^{-1}$. An interesting comparison between the 529.74- to 532.2 and >532.2-m

soil zones shows that measured stover production was similar in the two areas, whereas grain yields were 15% less in the elevation zone >532.2 m. The lower harvest index in the >532.2-m than the 529.74- to 532.2-m elevation zone was attributed to differential water stress, which was higher in summit than footslope areas (Clay et al., 2001b, 2003).

The estimated average amount of nonharvestable soybean C returned to soil increased with root/shoot ratio (Table 2). For the moderate root/shoot ratio, the estimated amount of C returned to the soil by corn was 1.5 times more than that returned by soybean. This value was similar to the 1.4 ratio (corn/soybean returned) reported by Huggins et al. (1998).

The Δ values of organic materials returned to the soil were influenced by landscape position (Clay et al., 2001b, 2003). The landscape dependence of the Δ values was the direct result of water stress. In corn, water stress increased Δ values while the opposite was true for soybean. For example, stover Δ values in 2001 and 2002 averaged 3.5, 3.6, 3.75, 3.8, and 3.92‰ in the <523.4-, 523.4- to 527.1-, 527.1- to 529.7-, 529.7- to 532.2-, and 532- to 534.3-m elevation zones, respectively. Soybean grain had different results and in 2000 averaged 19.93, 19.75, 19.4, 19.2, and 18.7‰ in the <523.4-, 523.4- to 527.1-, 527.1- to 529.7-, 529.7- to 532.2-, and 532- to 534.3-m elevation zones, respectively.

Soil Organic Carbon Mineralization Kinetics

Nonisotopic Maintenance Rate Calculations

To maintain soil productivity, the amount of postharvest residues returned to soil must exceed the maintenance rate (Bolinder et al., 1999; Ortega et al., 2002; Prakash et al., 2002). Elevation zone did not influence the relationship between NHC/SOC and dSOC/dt . For the moderate root/shoot ratio, the whole-field linear relationship between NHC/SOC and dSOC/dt was $\text{NHC}/\text{SOC} = \text{dSOC}/\text{dt}(2.66 \times 10^{-5} \pm 1.22 \times 10^{-5}) + 0.121 (\pm 0.004)$, $r = 0.55$ at $P = 0.01$. This relationship suggests that to maintain SOC levels in the 0- to 15-cm soil depth, 12% of the SOC or 6200 kg NHC ha^{-1} must be applied annually. Root/shoot ratios influenced the maintenance rates and the k_{SOC} and k_{NHC} values calculated from the y intercept and slope values. Calculated maintenance rates were proportionally related to the estimated NHC returned to soil, i.e., the higher the root/shoot ratio, the higher the estimated maintenance rate. Findings from this analysis showed that accurate estimates of belowground biomass and the influence of residue placement on mineralization rates are required to determine maintenance rates.

Data from Allmaras et al. (2004) were used to test the feasibility of using Eq. [6] to assess C dynamics in a system where belowground biomass is better understood. In this study, C inputs and changes in SOC levels during a 13-yr period were measured. Tillage treatments were no-tillage, moldboard plow, and chisel plow. Nitrogen was applied at two rates (0 and 200 kg N ha^{-1}) and stover was either removed or left in place. The statistically significant (0.01 level) model relating NHC and

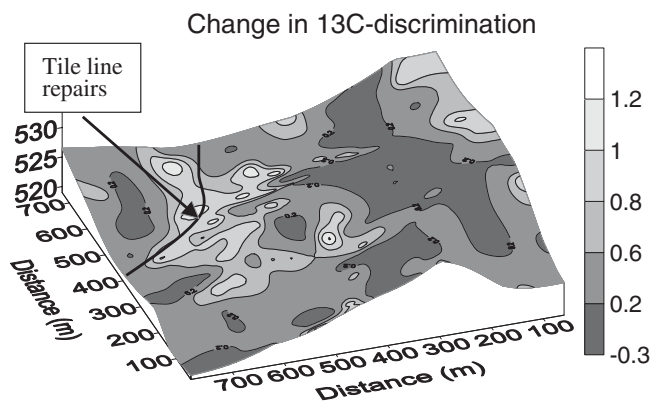


Fig. 3. The change in soil ^{13}C discrimination (‰) from 1995 to 2003.

Table 2. The influence of elevation zone on the average annual amount of biomass C returned to soil or harvested. For corn, grain and stover yields were experimentally measured and nonharvested (crown, roots, exudates) estimates were based on root/shoot ratios of 0, 0.4 (low), 0.8 (moderate), and 1.5 (high). For soybean, grain was measured, residue returned was calculated from a 0.35 harvest index, and root biomass was estimated with root/shoot ratios of 0, 0.4 (low), 1.0 (moderate), and high (1.5).

Elevation zone	Corn					Soybean				
	Grain	Root/shoot ratio				Grain	Root/shoot ratio			
		None	Low	Moderate	High		None	Low	Moderate	High
m		— kg C ha ⁻¹ yr ⁻¹ —					— kg C ha ⁻¹ yr ⁻¹ —			
<523.4	2870	2740	4450	6690	12 200	910	2190	3320	4340	5190
523.4–527.3	3000	2750	4500	6800	12 630	840	2020	3040	3990	4810
527.3–529.7	2800	2610	4300	6470	11 790	830	1830	2970	3940	4750
529.7–532.2	2760	2430	4030	6110	11 020	800	1830	2880	3810	4590
532.2–534.3	2350	2470	3980	5880	10 610	730	1590	2620	3480	4190
Whole field	2750	2540	4170	6290	11 530	810	1910	2930	3850	4630

SOC was $\text{NHC/SOC} = 0.0644(\pm 0.015) - (2.72 \times 10^{-5} \pm 2.36 \times 10^{-5})(\text{dSOC}/\text{dt})$. Based on this equation: (i) it was estimated that the annual maintenance rate for this soil was $6200 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ ($0.0644 \times 96250 \text{ kg C ha}^{-1}$); (ii) $39\% [=100 \times 1/(96250 \times 2.72 \times 10^{-5})]$ of the non-harvested biomass was mineralized in the first year after application, and (iii) $2.51\% (=100 \times 0.0644 \times 0.39)$ of the SOC was mineralized annually. This maintenance rate was consistent with values reported in the literature (Kaboneka et al., 1997). Jenkinson and Rayner (1977) reported that in Rothamsted, England, 1200 to 1900 $\text{kg C ha}^{-1} \text{ yr}^{-1}$ from wheat (*Triticum aestivum* L.) straw was sufficient to maintain SOC levels. In Iowa, Larson et al. (1972) estimated that 1.9% of SOC was mineralized annually and that annual applications of 6000 $\text{kg biomass ha}^{-1}$ ($\sim 2500 \text{ kg C ha}^{-1}$) are needed to maintain SOC levels. Barber (1979) used changes in SOC during 12 yr in production and fallow fields to determine that 2.4% of the SOC was decomposed each year, 11% of the residue C was synthesized into new organic matter, and annual applications of at least 4000 kg C ha^{-1} were needed to maintain SOC levels at $17.4 \text{ g C kg}^{-1} \text{ soil}$. In Minnesota, Huggins et al. (1998) used a simulation model combined with changes in Δ to determine that annual applications of 5600 $\text{kg C ha}^{-1} \text{ yr}^{-1}$ are needed to maintain surface soil (0–15 cm) at $45\,000 \text{ kg C ha}^{-1}$.

Isotopic Approaches: Relative Proportion of C₃ and C₄ Plants in Soil Organic Carbon

Changes in the f values, as calculated with the equation $f = (\Delta_{\text{SOC}} - \Delta_{\text{C}_4})/(\Delta_{\text{C}_3} - \Delta_{\text{C}_4})$, from 1993 to 2003 suggest that: (i) the contribution of C₃ biomass to SOC generally decreased from 1993 to 2003; and (ii) the contribution from C₄ plants to SOC increased at elevation zones <527.3 m and remained unchanged at elevation zones >527.3 m (Fig. 4). These results were attributed to corn, a C₄ plant, being sown five times while soybean, a C₃ plant, was sown three times. If only C₃ or C₄ plants had been grown, this information would be very useful; however, in this case both C₃ and C₄ plants were grown and the mineralization kinetics were confounded.

Isotopic Approaches: Carbon Budgets

Five values, $\text{SOC}_{\text{soil retained}}$, $\text{SOC}_{\text{final}}$, $\text{SOC}_{\text{initial}}$, $\Delta_{\text{SOC retained}}$, and Δ_{PCR} were needed to calculate the effect of elevation

zone on C budgets (Eq. [11], [12], and [13]). To test the sensitivity of the approach to belowground biomass estimates, a range of root/shoot ratios were tested. The tested root/shoot ratios had minimal and inconsistent impact on Δ_{PCR} values and calculated C budgets.

For the moderate root/shoot ratio when $\epsilon = 0$, the amount of C mineralized and new C incorporated into the soil was related to the change in soil Δ values during 8 yr (Table 3). Elevation-zone differences in new C incorporated into SOC, the amount of C lost, and the percentage of C mineralized was determined (Table 3). More than twice as much new C was incorporated into $\text{SOC}_{\text{final}}$ in the 523.4- to 527.3-m elevation zone ($7420 \text{ kg C ha}^{-1}$) than the 527.3- to 529.3-m elevation zone ($2780 \text{ kg C ha}^{-1}$). During the study, approximately 14.9% of $\text{SOC}_{\text{initial}}$ in the 523.4- to 527.3-m elevation (14.9%) was mineralized, which was double the amount mineralized in the 527.3- to 529.7-m zone (7.6%). The difference between the net amount of SOC mineralized and new C incorporated indicates that there was a small loss of C ($460 \pm 416 \text{ kg C ha}^{-1}$) from the field. Landscape differences were attributed to: (i) water stress, which influenced root and shoot growth characteristics; (ii) runoff, which may have transported soil and crop residues from summit and shoulder areas to footslope areas; and (iii) tile-line repairs, which may have produced conditions that encouraged SOC mineralization. Other researchers have noted that

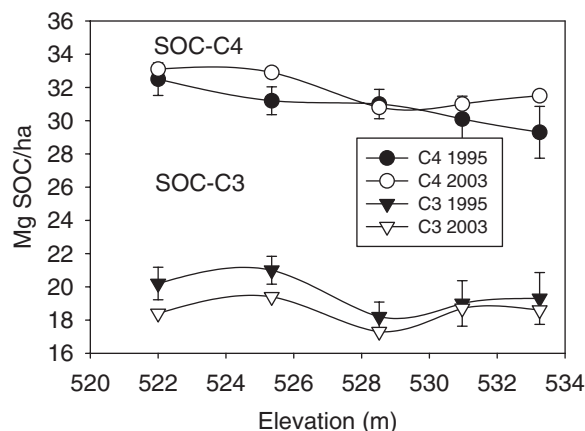


Fig. 4. The influence of sampling date and elevation zone on SOC (soil organic C) derived from C₃ and C₄ plants. Brackets represent the t value at the 0.1 significance level.

Table 3. The influence of elevation zone on the amount of soil organic C (SOC) contained in the soil in 1995, the change in ^{13}C discrimination (Δ) during the 8 yr of the study, the amount of relict SOC retained in the soil after mineralization, the amount of new C incorporated into SOC, and the amount of SOC mineralized. The 90% confidence intervals (CI) are shown.

Elevation zone	1995 soil organic C		Δ change		Original C retained		New C incorporated		Original C mineralized		C mineralized [†]	
	Mean	CI	Mean	CI	Mean	CI	Mean	CI	Mean	CI	Mean	CI
m	kg C ha ⁻¹		‰		kg C ha ⁻¹		kg C ha ⁻¹		kg C ha ⁻¹		%	
<523.4	52 600	960	0.50	0.084	44 040	1763	6230	990	8830	1800	16.6	3.45
523.4–527.3	52 200	870	0.51	0.066	44 200	1282	7420	940	7750	1370	14.9	2.61
527.3–529.7	49 130	1310	0.24	0.089	45 400	1963	2780	1000	3760	1450	7.6	2.89
529.7–532.2	49 080	1180	0.21	0.110	46 690	2078	2950	1490	2390	1330	4.9	2.75
532.2–534.3	48 760	2420	0.43	0.241	43 380	2905	6320	3400	5240	3720	7.6	5.63
Whole field	51 060	555	0.42	0.043	44 600	846	4590	460	5050	625	9.70	1.19

[†] Calculated as 100(mineralized C)/initial soil organic C.

management can influence C mineralization rates (Torbert et al., 2000; Halvorson et al., 2002; West and Post, 2002).

The different root/shoot ratios had almost identical impacts on calculated C budgets (data not shown). For example, the new C incorporated into SOC_{final} in 0- to 15-cm soil depth was 5800, 6900, 2600, 2700, and 5900 kg C ha⁻¹ for the high root/shoot ratio. These values were within 500 kg C ha⁻¹ of the values reported for the moderate root/shoot ratio (Table 3). For the isotopic approach, Δ_{NHC} , not root/shoot ratios, had a direct impact on calculated C budgets.

Sensitivity analysis showed that if ^{13}C discrimination during SOC mineralization occurred ($\epsilon = -2.52\text{‰}$), then the amount of SOC mineralization and new C incorporated into SOC were 3500 and 2840 kg C ha⁻¹, respectively. These findings suggest that, in C balance studies, ^{13}C discrimination during relict C mineralization should be measured. This can be accomplished by including plots where plant growth is prevented.

CONCLUSIONS

Using previous C budget analysis approaches, the landscape dependency of the cropping system could not be directly assessed. Fractionating the soil into C₃ and C₄ components produced inconclusive results (Allmaras et al., 2004), and the approach requiring the maintenance of numerous reference sites at numerous landscape positions, as explained by Balesdent and Mariotti (1996) and Balesdent et al. (1988), was not practical. This study provides an alternative approach to assess SOC dynamics in fields containing substantial variability. The nonisotopic approach, using moderate root/shoot ratios, estimated that 6200 kg C ha⁻¹ was required for SOC maintenance. Calculated maintenance rates were directly proportional to estimated NHC and root/shoot ratios.

Equations [11], [12], and [13] have distinct differences from the equations used to calculate f (Allmaras et al., 2004) and F (Balesdent and Mariotti, 1996). First, ^{13}C discrimination during mineralization can be integrated, if necessary, into the calculations. Second, Eq. [11], [12], and [13] do not require a reference site and spatial variability was implicitly considered. Third, absolute values rather than relative values were calculated. Fourth, the approach can be used to estimate C budgets for systems containing both C₃ and C₄ plants.

The modified ^{13}C natural abundance approach was used to quantify landscape effects on SOC mineralization kinetics. Sensitivity of the modified Δ approach showed that the effect of simulated root/shoot ratios was limited to its effect on calculated Δ_{PCR} values, and therefore had a minimal impact on calculated C budgets. For this approach to provide accurate estimates of C budgets, accurate estimates of $\Delta_{\text{SOC final}}$ and Δ_{PCR} are required. Because these values cannot be measured directly, they can be estimated using the Rayleigh fractionation equation. If ^{13}C discrimination during SOC mineralization did not occur ($\epsilon = 0$), then in the <527.3- and >527.3-m elevation zones, 15.3 and 6.7%, respectively, of the SOC_{initial} were mineralized during the study. Sensitivity analysis showed that if $\epsilon < 0$ (^{13}C discrimination during mineralization), then SOC_{initial} mineralization would have been less. The potential effects of ^{13}C discrimination during mineralization on SOC budgets and related half-lives need to be investigated. Landscape differences were attributed to: (i) water stress, which influenced root and shoot growth characteristics; (ii) runoff that may have transported soil and crop residues from summit and shoulder areas to footslope areas; and (iii) tile-line repairs, which may have produced conditions that stimulated SOC mineralization.

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